

RESIN COMPOSITION FOR TRANSPARENT THIN MEMBRANE AND ITS CURED MATERIAL

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Report a data error here**Abstract of JP2000248052**

PROBLEM TO BE SOLVED: To obtain the subject composition excellent in preservation stability, and showing less process soiling in its use and a good working efficiency by containing a compound containing glycidyl group and a compound containing an acid anhydride. **SOLUTION:** This resin composition is obtained by containing (A) a compound having preferably 5,000-1,000,000 weight-average molecular weight (based on a polystyrene, using a gel permeation chromatography method) and 150-2,000 g/eq epoxy equivalent (JIS K-7236), (e.g.; a high molecular weight epoxy resin) with (B) a compound having preferably 500-500,000 weight-average molecular weight (based on a polystyrene) and containing an acid anhydride in a ratio of (the epoxy equivalent of the component A)/(the acid anhydride equivalent of the component B)=0.2-5. As the component B, a (co)polymer having a compound such as maleic anhydride, itaconic acid anhydride, himic acid anhydride, succinic acid anhydride, etc., as a constituting unit is cited.

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(54)【発明の名称】 透明薄膜用樹脂組成物及びその硬化物

(57)【要約】

【課題】保存安定性に優れ、工程汚染が極めて少なく、硬化膜が耐熱性、耐薬品性、耐水性、防染性、密着性に優れ、LCDやCCDに用いられるカラーフィルターの製造に有用な透明薄膜用樹脂組成物を提供する。

【解決手段】グリシル基を有する高分子(A)と酸無水物を有する高分子(B)を含有する透明薄膜用樹脂組成物。

【特許請求の範囲】

【請求項1】グリシジル基を有する高分子(A)と酸無水物を有する高分子(B)を含有する透明薄膜用樹脂組成物。

【請求項2】グリシジル基を有する高分子(A)の重量平均分子量が5,000~1,000,000であり、エポキシ当量(WPE)が150~2,000である請求項1記載の透明薄膜用樹脂組成物。

【請求項3】酸無水物を有する高分子(B)の重量平均分子量が500~500,000である請求項1又は2に記載の透明薄膜用樹脂組成物。

【請求項4】請求項1乃至3のいずれか一項に記載の透明薄膜用樹脂組成物の硬化物。

【請求項5】請求項4に記載の硬化物の層を有する固体撮像素子。

【請求項6】請求項4に記載の硬化物の層を有するカラーフィルター。

【請求項7】請求項6に記載のカラーフィルターを有するカラー液晶表示装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、透明薄膜用樹脂組成物及びその硬化物に関するものであり、特に液晶表示装置等のカラー化に必要なカラーフィルター、カラーCCD(電荷結合素子)を代表とする固体撮像素子の平坦化層やその上に設けられるカラーフィルター部の中間層、保護層を形成する材料として有用な透明薄膜用樹脂組成物に関するものである。

【0002】

【従来技術】パソコン、カーナビゲーションシステム、液晶テレビ等のカラー表示に用いるカラー液晶表示装置、また、カラービデオカメラ、デジタルカメラ、カラーコピー機、医療機器の画像処理装置等の入力デバイスとして用途の広がる電荷結合素子を代表とする固体撮像素子には、固体撮像素子表面受光部や回路配線部等による凹凸を緩和する目的で平坦化層、カラーフィルターが設けられている。この平坦化層やカラーフィルターに設けられる所定の形状にバーニングされたカラー画素上の保護層、染色法カラーフィルターに於ける混色防止の為の防染中間層、各カラー画素の表面を保護する目的の保護層には、透明薄膜が形成されている。

【0003】従来、この様な平坦化層、中間層、保護層用の樹脂としては、感光性樹脂、エポキシ樹脂等が用いられている。ネガ型感光性樹脂では、低分子モノマーを紫外線照射して架橋させ不溶化させるが、得られた薄膜はベースになる材料が低分子である事や架橋密度が充分得られない事から、又、一方ポジ型感光性樹脂では、架橋の無い直鎖型高分子であるので、それらによって得られた薄膜の耐熱性、耐薬品性、耐水性や機械的強度等は通常の熱硬化性樹脂より得られた薄膜より劣る為に、高

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温蒸着によりITO等の透明電極を形成する際に膜の色変、皺寄せを引き起こし、カラーフィルターの品質を著しく低下させることがあった。

【0004】又、耐熱性に優れる為広く用いられてきたエポキシ系樹脂としては、硬化剤に低分子量のアミン、酸無水物、イミダゾール類が使用されているので、これらの組成物は、ポットライフが短く取り扱いに制約がある事、又は塗布直前に主剤と硬化剤の2液を混合する必要があった。又、低分子量の硬化剤が熱硬化時に揮発しラインやデバイスを汚染してしまう等の工程汚染という問題が起り、生産性やコスト面、環境面で多大な悪影響を及ぼしている。更に、スループット向上の必要性に伴うポストベイク時間の短縮化により、この組成物でCCDの平坦化膜、カラーフィルターの中間膜、保護膜を形成した場合、硬化が不十分な為、未反応な硬化剤が、次工程で溶出してしまう欠点をも抱えている。

【0005】一方、従来の代表的なCCD用染色法カラーフィルターは、撮像素子上に平坦化を目的としたボリマー層を形成後、その上にバターン化した染色層を設け次いで透明な防染中間層を形成させ、その上に同様にして次の染色層を形成するという工程を繰り返す事により作成されている。この中間層を形成する樹脂としては、(メタ)アクリル酸グリシジルと(メタ)アクリル酸2-ヒドロキシエチル及び桂皮酸クロリド又はその誘導体の反応物と、ラジカル共重合させた高分子(特開昭61-180235号)や、ポリメチルメタクリレート等が知られているがこれらから形成した中間層では、前者高分子では染色層間の混色が生じたり、後者高分子では染色層との接着性が劣る為に、共に実用性の高い中間層を得ることが出来ない。

【0006】

【発明が解決しようとする課題】本発明は、保存安定性に優れ、使用時の工程汚染が極めて少なく、作業性の良好な透明薄膜用樹脂組成物を提供し、更に耐熱性、耐薬品性、耐水性、防染性、密着性に優れた透明薄膜用樹脂組成物の硬化物を提供する事を目的とする。

【0007】

【課題を解決する為の手段】本発明は(1)グリシジル基を有する高分子(A)と酸無水物を有する高分子(B)を含有する透明薄膜用樹脂組成物、(2)(A)が重量平均分子量5,000~1,000,000、エポキシ当量(WPE)が150~2,000である(1)記載の透明薄膜用樹脂組成物、(3)(B)が重量平均分子量500~500,000である(1)又は(2)記載の透明薄膜用樹脂組成物、(4)(1)乃至(3)のいずれか一項に記載の透明薄膜用樹脂組成物の硬化物、(5)(4)に記載の硬化物の層を有する固体撮像素子、(6)(4)に記載の硬化物の層を有するカラーフィルター、(7)(6)に記載のカラーフィルターを有するカラー液晶表示装置、に関する。

【0008】

〔発明の実施の形態〕本発明の透明薄膜用樹脂組成物は、グリシジル基を有する高分子（A）と酸無水物を有する高分子（B）を含有する。本発明に使用される（A）成分としては、エチレン性不飽和基とグリシジル基を有するモノマーの（共）重合体や高分子量のエポキシ樹脂が好ましい。（A）成分の重量平均分子量（M W）は、ポリスチレン換算で5,000～1,000,000、好ましくは30,000～500,000である。MWの異なる2種以上の（A）成分を組み合わせることによって、組成物の粘度を調節することも出来る。重量平均分子量はゲルバーミエーションクロマトグラフィー（G P C）法により測定される。MWが5,000未満の場合、硬化膜は耐薬品性、耐水性に劣り実用水準で使用するのは困難である。MWが1,000,000を超える場合、硬化膜の機械的強度、耐薬品性、耐水性は増すものの、樹脂組成物が著しく高粘度となる為に薄膜化に困難を来す。また、（A）成分のエポキシ当量（W P E）は、150～2,000 g / eq が好ましく、更に好ましくは150～750 g / eq である。エポキシ当量は、J I S K - 7 2 3 6 の方法で測定される。

【0009】（A）成分の（共）重合体の構成成分であるエチレン性不飽和基とグリシジル基を有するモノマーとしては、例えば（メタ）アクリル酸グリシジル、 α -エチルアクリル酸グリシジル、 α -n-ブロビルアクリル酸グリシジル、 α -n-ブチルアクリル酸グリシジル、（メタ）アクリル酸-3,4-エポキシブチル、（メタ）アクリル酸-4,5-エポキシベンチル等のエステル部分にグリシジル基を有するアクリル酸エステル、アリルグリシジルエーテル、p-ビニル安息香酸グリシジル、メチルグリシジルイタコナート、エチルグリシジルマレート、ビニルグリシジルスルホナート、グリシジル- β -ビニルアクリレート、グリシジルソルベート等のグリシジルジエンカルボキシレートや、グリシジル基を持つジエノフィル化合物とジエン化合物をD i e l s - A l d e r 反応させる事によって得られる反応性モノマー等が挙げられる。

【0010】エチレン性不飽和基とグリシジル基を有するモノマーと共に重合可能なモノマーとしては、例えばエチレン性不飽和基を有するモノマーが挙げられる。具体的には、例えば、（メタ）アクリル酸アルキルエーテル、（メタ）アクリル酸ジシクロベントニル、フマル酸アルキルエーテル、スチレン、 α -アルキルスチレン、

アクリロニトリル、イソブチレン、ブタジエン、イソブレン、酢酸ビニル、ジビニルブチラール等が挙げられる。

【0011】（A）成分の高分子量のエポキシ樹脂としては、例えばビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂、ビスフェノールS型エポキシ樹脂、ノボラック型エポキシ樹脂、グリシジルエーテル系エポキシ樹脂が挙げられる。

【0012】これら（A）成分は、単独で用いても2種以上混合して用いても良い。

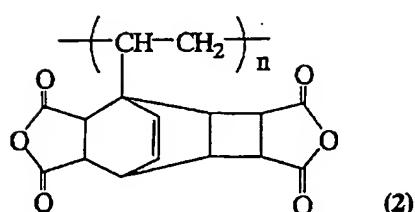
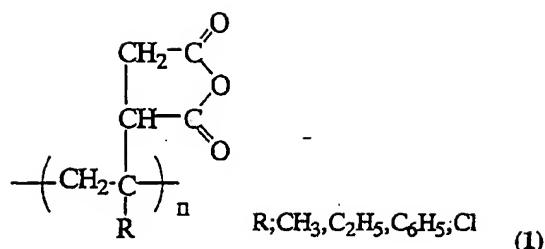
【0013】これらの内、本用途の要求特性である透明性、耐熱変色性、染色時防染性に優れるものとして特に好ましい高分子としては、（メタクリル酸グリシジル）-（メタクリル酸アルキルエーテル）共重合体、（メタクリル酸グリシジル）-（スチレン）共重合体、（メタクリル酸グリシジル）-（メタクリル酸アルキルエーテル）-（スチレン）共重合体である。アルキル鎖の炭素数は、1～8個、好ましくは1～3個である。この化合物の例としては、マーブルーフG-2050M、G-870S、G-1010S、ブレンマーCP-510SA（何れも日本油脂製、商品名）等がある。

【0014】本発明に使用される（B）成分としては、マレイン酸無水物、イタコン酸無水物、ハイミック酸無水物、コハク酸無水物、シトラコン酸無水物、アクリル酸無水物、メタクリル酸無水物等より1種又は2種以上選択される化合物を構成単位とする（共）重合体が挙げられる。又、これらと共に重合可能な不飽和二重結合を有する化合物としては、エチレン類、プロピレン類、ブテン類、ブタジエン類、高級オレフィン類、スチレン類、

30 スチルベン類、酢酸ビニル、アリルエーテル、1-メチルシクロプロパン、環状ジエン化合物、ジシクロジエン化合物等が挙げられ、交互性の良好な共重合体が得られる。又、三級水素を持つポリエンポリマーとマレイン酸無水物、ビロメリット酸無水物、トリメリット酸無水物、ベンゾフェノンテトラカルボン酸無水物、メタクリル酸無水物、エチレングリコールビストリメリテート、グリセリントリメリテート等の酸無水物を反応させて酸無水物構造を導入した高分子化合物が挙げられる。例えば、下記化学式（1）の化合物（工化、70, 1432, '67）、下記化学式（2）の化合物（Pure Appl. Chem., 34, 305, '73）を挙げることが出来る。

【0015】

【化1】



【0016】(B)成分の重量平均分子量(MW)は、
ポリスチレン換算で500~500,000、好ましく
は500~300,000である。

【0017】これら(B)成分は、単独で用いても2種
以上混合して用いても良い。

【0018】本発明の透明薄膜用樹脂組成物の(A)、
(B)成分の配合量は、硬化物の物性から配合比を決定
しても良いが、(A)のWPEと(B)の無水酸当量の
関係が、WPE/無水酸当量 = 0.2~5の範囲が好ま
しい。(A)成分に対し(B)成分の配合量が極端に少
ないと、硬化物に充分な硬度が得られなかったり、機械
衝撃性が低下する等の問題を生ずる。一方、(A)成分
に対し(B)成分の配合量が極端に多い場合、酸無水物
が大気中の水分を吸湿し易く、硬化不足の傾向を来す
他、硬化物の白濁等不具合を生ずる為、適当でない。

【0019】本発明の透明薄膜用樹脂組成物は必要によ
り、硬化促進剤としてポリアミド類、メラミン誘導体を
添加しても良い。使用量は加熱硬化時に大量揮発しない
程度であることが好ましく、(A)、(B)合計固形分
に対し10%以下が好ましい。

【0020】本発明の透明薄膜用樹脂組成物は、溶媒に
溶解させた塗布液として調製するのが好ましい。用いる
溶媒としては樹脂組成物と化学反応を起こす恐れが無い
限り特に制限はなく、例えばエチル系、エーテル系、
ケトン系、芳香族炭化水素系等の有機溶剤が挙げられ
る。

【0021】具体的には、酢酸アルキルエステル、プロ
ピオン酸アルキルエステル、酪酸アルキルエステル等の
飽和脂肪族モノカルボン酸アルキルエステル類、乳酸ア
ルキルエステル類、アルコキシ酢酸アルキルエステル
類、2-オキシプロピオン酸アルキルエステル類、2-アル
コキシプロピオン酸アルキルエステル類、3-オキ

シプロピオン酸アルキルエステル類、3-アルコキシブ
ロピオン酸アルキルエステル類、2-オキシ-2-メチ
ルプロピオン酸アルキルエステル類、2-アルコキシ-
2-メチルプロピオン酸アルキルエステル類、ビルビン
酸アルキルエステル、アセト酢酸アルキルエステル、2-
オキソブタノン酸アルキルエステル等のケトン酸エス
テル類、ジアルキルエーテル、テトラヒドロフラン、ジオ
キサン等のエーテル類、ジエチレングリコールモノメチ
ルエーテル、ジエチレングリコールモノエチルエーテ
ル、ジエチレングリコールモノブチルエーテル、エチ
レングリコールモノメチルエーテル、エチレングリコール
モノエチルエーテル、エチレングリコールモノブチルエ
ーテル、エチレングリコールモノイソプロピルエーテ
ル、プロピレングリコールモノメチルエーテル、プロピ
レングリコールモノエチルエーテル等のグリコールエ
ーテル類及びそのアセテートのグリコールエーテルアセ
ート類、メチルエチルケトン、シクロヘキサン、2-
ヘプタノン、3-ヘプタノン等のケトン類、キシレン、
トルエン等の芳香族炭化水素類等が挙げられる。これら
溶媒は、単独で用いても2種以上混合して用いても良
い。

【0022】本発明の透明薄膜用樹脂組成物を調製する
際、塗膜の物性を向上させる為に、表面平滑剤、基板密
着改良材、界面活性剤等の調整添加剤を加えても良い。
具体的には、バーフルオロアルキル系化合物、シリコン
系化合物、ポリオキシエチレン化合物、ポリオキシブロ
ピレン系化合物、長鎖アルキル化合物等が挙げられる。

【0023】本発明の透明薄膜用樹脂組成物を調製する
には、例えば上記溶剤中に(A)、(B)成分を、更に
所望により硬化促進剤や添加剤を加え、均一に混合溶解
すればよい。溶液中の(A)成分と(B)成分の合計濃
度は、3~30重量%、好ましくは、5~20重量%程

度である。

【0024】本発明の硬化物は通常、所定の基材に塗布し、加熱焼成することによって、膜厚0.05~5μm程度の透明薄膜として形成される。透明薄膜を形成すべき基材としては、例えば、硝子類、ポリカーボネート類、フィルム類、撮像素子の形成されたシリコンウェハー、LCD又はCCD用カラーフィルターのパターン化された着色樹脂膜、印刷用紙、印刷用繊維、金属板等が挙げられる。塗工方法としては、樹脂組成物溶液を目的の基材上に、スピンドルコート法、ロールコート法、バーコート法、印刷法、浸漬法、スプレイ法等の方法で塗布する。続いて、60~120°Cに設定されたホットプレート又はコンベクションオーブンにて1~10分程度予備乾燥後、180~250°Cにて3~30分程度加熱焼成し、硬化膜を得る。

【0025】本発明のカラーフィルターは、上記組成物の硬化膜を有する。このカラーフィルターは、カラー液晶表示装置、カラーCCD用に用いられる。液晶表示装置用カラーフィルターの製造は、公知の方法で行われる。例えば、硝子基板上にフォトリソグラフィー法、印刷法、電着法等によって、赤、青、緑の着色画素及びブラックマトリクスを作成後、その上に透明保護膜を形成し、更にITOの透明導電膜（電極）を積層することによって得られる。このカラーフィルターを表示面に配置することにより、本発明のカラー液晶表示装置が得られる。

【0026】本発明の固体撮像素子は、撮像素子の形成されたシリコンウェハーに、直接もしくは他の層を介して上記の透明薄膜用樹脂組成物の硬化物の層を設けたものである。その製法は、予め硝子基板上に上記の透明薄膜用樹脂組成物の硬化物の層を有するカラーフィルターを形成しこれをチップサイズに切断してCCDチップ上に位置合わせ後、接着剤で貼り合わせる方法と、光電変換素子や電荷転送素子等で成る固体撮像装置が形成されたシリコン基板上に、シリコンウェハー表面の凹凸の平*

表1

| | (A) 群 | MW | WPE | (B) 群 | MW | |
|-----|-----------|---------|------|-------|-----------|---------|
| a 1 | G-2050M | 225,000 | 340 | b 1 | GSM-1001 | 10,000 |
| a 2 | -GMA-MMA- | 100,000 | 240 | b 2 | GSM-6001 | 60,000 |
| a 3 | -GMA-BMA- | 300,000 | 1000 | b 3 | GSM-10001 | 100,000 |
| a 4 | -GMA-AN- | 150,000 | 500 | b 4 | 式(1) | 50,000 |
| a 5 | -GMA-ST- | 400,000 | 2500 | b 5 | 式(2) | 25,000 |

【0031】但し、GMA：グリジルメタクリレート、MMA：メチルメタクリレート、G-2050M：GMA-MMA共重合体（日本油脂製、商品名）、BM A：ブチルメタクリレート、AN：アクリロニトリル、ST：ステレン、GSM-1001：ステレン-マレイン酸無水物1:1共重合体（岐阜セラック製、商品名）※

* 滑化の為に上記の透明薄膜用樹脂組成物の硬化物の層を形成し、次に染色法又は顔料分散フォトリソグラフィー法等によって直接カラーフィルターを形成し、カラーフィルター完成後チップに切断するオンチップ法がある。位置合わせ精度、量産性に優れる後者の製造方法が主流となっている。前者の方法に於けるカラーフィルターは、LCD用カラーフィルターの製法と同様である。後者の製法は、まずシリコンウェハー表面の凹凸の平滑化の為に透明薄膜を形成し、次に染色法でカラー画素を作成する場合は各色染色後に防染目的の透明薄膜を形成し、最後のカラー画素染色後に透明薄膜によって保護層を設けることによってCCDのカラーフィルターが完成する。

【0027】本発明の透明薄膜用樹脂組成物は、上記の様にして加熱処理をする事によって、前記(A)成分と(B)成分とが架橋し合い超高分子量化する為、得られた透明薄膜は、耐熱性、耐薬品性、耐水性、耐染色性、密着性に優れており、LCD用カラーフィルター等の着色樹脂膜の保護層、又はCCDの平坦化層、及び中間層及び保護層の形成に際し特に有用となる。又、低分子化合物を含まないので、揮発、溶出等工程汚染が極めて少ない信頼性の高い透明薄膜を得、これによって得られたカラーフィルターを使用した液晶表示装置、固体撮像素子は優れた表示品位を確保する事が出来るのである。

【0028】

【実施例】実施例によって本発明を更に具体的に説明するが、本発明がこれらの実施例のみに限定されるものではない。

【0029】実施例1~10

表1に示す(A)群の共重合高分子化合物と、(B)群の高分子化合物を各々表2に示す比でプロピレングリコールモノメチルエーテルアセテートに固形分11重量%となるように溶解し透明薄膜用樹脂組成物を調製した。

【0030】

※名)、GSM-6001：ステレン-マレイン酸無水物1:1共重合体（岐阜セラック製、商品名）、GSM-10001：ステレン-マレイン酸無水物1:1共重合体（岐阜セラック製、商品名）を表す。

【0032】

表2

| 実施例 | a 1 | a 2 | a 3 | a 4 | a 5 | b 1 | b 2 | b 3 | b 4 | b 5 |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|

| | | | | | | | |
|----|----|----|----|----|----|---|----|
| 9 | | | | | | | 10 |
| 1 | 10 | | | 3 | | | |
| 2 | | 10 | | | 4 | | |
| 3 | | | 10 | | | 2 | |
| 4 | | | | 10 | | | 3 |
| 5 | | | | | 10 | | 2 |
| 6 | 10 | | | | | 2 | |
| 7 | | 10 | | | | 3 | |
| 8 | | | 10 | | | 2 | |
| 9 | | | | 10 | | | 3 |
| 10 | 10 | | | | | 3 | |

(固形重量比)

【0033】この各種透明薄膜用樹脂組成物により得られた硬化膜の耐溶剤性、耐水性、耐熱性、色被り、残渣汚染の評価を以下に記すように行った。評価結果を表5に示す。

【0034】透明薄膜用樹脂組成物の硬化膜の作成例
ガラス基板上に最終膜厚0.5 μmとなるよう塗布し、表面温度100°Cのホットプレート上で100秒間予備乾燥後、200°Cのホットプレート上で5分間加熱し、透明薄膜を得た。これを各種試験片とする。

【0035】耐溶剤性：上記試験片を、下記溶剤に各種条件で処理、試験前後の膜厚を測定し残膜率を求め、膜面を光学顕微鏡で観察した。

①60°C IPA (イソプロパノール) 蒸気×20分曝露
②50°C NMP (N-メチルピロリドン) ×20分浸漬
③50°C GBL (γ-ブチロラクトン) ×20分浸漬

【0036】耐水性：純水の入ったプレッシャークッカー試験 (PCT) 用容器に上記試験片を入れ130°Cにて3時間処理を行い、膜面を光学顕微鏡で観察した。

【0037】耐熱性：上記試験片を、250°Cのホット*30 【0040】

* プレートで60分間加熱処理し加熱前後の着色度 ($\Delta E * ab$ 値：色度差) を分光光度計にて測定した。

【0038】色被り、残渣汚染：上記の透明薄膜上に、顔料分散カラーネガレジスト KAYAMIRROR D CF-G630 (緑色顔料レジスト：日本化成製、商品名) を約1 μm相当膜厚に塗布し、80°Cのホットプレート上で100秒間プレベイク後、紫外線未照射のまま KAYAMIRROR DVL-T50D (有機アルカリ系現像液；日本化成製、商品名) にて全面現像し、水洗乾燥後透明薄膜上への色被り ($\Delta E * ab$ 値) を分光光度計にて測定した。又、残渣汚染を顕微鏡にて評価した。

【0039】比較例1～3

表3に示す熱硬化性樹脂と硬化剤を組み合わせた透明薄膜用樹脂組成物として、表4に示す配合比で固形分11重量%となるように溶媒に溶解した。耐溶剤性、耐水性、耐熱性、色被り、残渣汚染の評価を上記と同様に行った。評価結果を表5に示す。

表3

| | 熱硬化性樹脂 | MW | WPE | 硬化剤 |
|------|---------------------|---------|-----|--------------------|
| c1 | -CMA-MMA- | 100,000 | 240 | d1 無水トリメリット |
| 酸 | | | | |
| c2 | -CMA-MMA- | 225,000 | 340 | d2 テトラヒドロ無水 |
| フタル酸 | | | | |
| c3 | -MAA-(N-フェニルマレイミド)- | 10,000 | 300 | d3 IRGANOX 3114 |

【0041】但し、IRGANOX 3114；トリス-(3,5-ジ-*t*-ブチル-4-ヒドロキシベンジル)※40 【0042】

表4

| 比較例 | c1 | c2 | c3 | d1 | d2 | d3 |
|-----|----|----|----|----|----|-----|
| 1 | 10 | | | 1 | | |
| 2 | | 10 | | | | 1.5 |
| 3 | | | 10 | | 1 | 0.5 |

(固形重量比)

【0043】

表5

| 実施例 | 耐溶剤性(残膜率) | | 耐水 △*ab | 耐熱 △E*ab | 色被り 残渣 |
|-----|-----------|-----|------------|-------------|-----------|
| | IPA | NMP | | | |

11

12

| | | | | | | | | | |
|---|------|------|------|---|----|---|----|---|----|
| 1 | 100% | 100% | 100% | 何 | 0. | 1 | 0. | 1 | 無し |
| 2 | 100% | 100% | 100% | れ | 0. | 2 | 0. | 1 | 無し |
| 3 | 100% | 100% | 100% | も | 0. | 3 | 0. | 1 | 無し |
| 4 | 100% | 100% | 100% | 変 | 0. | 4 | 0. | 1 | 無し |
| 6 | 100% | 100% | 100% | 化 | 0. | 1 | 0. | 1 | 無し |
| 7 | 100% | 100% | 100% | 無 | 0. | 2 | 0. | 1 | 無し |
| 8 | 100% | 100% | 100% | じ | 0. | 2 | 0. | 1 | 無し |

比較例

| | | | | | | | | | |
|---|-----|-----|-----|----|----|---|----|---|----|
| 1 | 82% | 85% | 80% | 白化 | 0. | 8 | 3. | 5 | 有り |
| 2 | 88% | 80% | 85% | 白化 | 0. | 7 | 5. | 7 | 有り |
| 3 | 77% | 70% | 72% | 白化 | 2. | 0 | 6. | 8 | 有り |

【0044】実施例11

上記の透明薄膜用樹脂組成物を、撮像素子の配設されたシリコンウェハー上に最終膜厚0.3μmとなるよう塗布し、表面温度100°Cのホットプレート上で100秒間予備乾燥後、200°Cのホットプレート上で5分間加熱し、下地平坦化膜を得た。この下地平坦化膜上に、顔料分散カラーネガレジストKAYAMIRROR DC F-G630（緑色顔料レジスト；日本化薬製、商品名）を約1μm相当膜厚に塗布し、80°Cのホットプレート上で100秒間ブレペイク後、所定のバターンフォトマスクを介して150mJ（365nm）の紫外線を照射した。続いてKAYAMIRROR DVL-T50D（有機アルカリ系現像液；日本化薬製、商品名）にて現像、水洗乾燥後、200°Cのホットプレート上で5分間ポストペイクし緑色微細画素を形成した。次いで、顔料分散カラーネガレジストKAYAMIRROR DC F-R630（赤色顔料レジスト；日本化薬製、商品名）を約1μm相当膜厚に塗布し、80°Cのホットプレート上で100秒間ブレペイク後、所定のバターンフォトマスクを介して150mJ（365nm）の紫外線を照射した。続いてKAYAMIRROR DVL-T50D（有機アルカリ系現像液；日本化薬製、商品名）にて現像、水洗乾燥後、200°Cのホットプレート上で5分間ポストペイクし赤色微細画素を形成した。次いで、顔料分散カラーネガレジストKAYAMIRROR DC F-B630（青色顔料レジスト；日本化薬製、商品名）を約1μm相当膜厚に塗布し、80°Cのホットプレート上で100秒間ブレペイク後、所定のバターンフォトマスクを介して150mJ（365nm）の紫外線を照射した。続いてKAYAMIRROR DVL-T50D（有機アルカリ系現像液；日本化薬製、商品名）にて現像、水洗乾燥後、200°Cのホットプレート上で5

分間ポストペイクし赤色微細画素を形成し、カラーフィルターが直付けされた固体撮像素子が得られた。これを顕微鏡により直上から観察したところ、下地平坦化膜上への色被り、残渣汚染は全く認められなかった。

【0045】実施例12

ガラス基板上に、顔料分散カラーネガレジストKAYAMIRROR DCF-R630、DCF-G630、DCF-B630（赤、緑、青色顔料レジスト；日本化薬製、商品名）を用いて実施例11と同様の方法で赤、緑、青の画素をバターン形成した着色樹脂膜上に、実施例1～10の透明薄膜用樹脂組成物により、保護膜として透明薄膜を形成し、LCD用カラーフィルターを作成した。各保護膜の密着性をクロスカット剥離試験によって評価したところ、何れも剥離数0／100で強固な密着性を確認した。又、これらのカラーフィルター上に250°Cにて30分かけ1TΩの蒸着操作を施したが、何れも敏銳現象は見られなかった。

【0046】

【発明の効果】本発明の透明薄膜用樹脂組成物を使用することにより、耐熱性、耐薬品性、耐水性、耐染色性、密着性に優れた透明薄膜を簡便に製造することが出来る。LCD用カラーフィルターの着色樹脂膜の保護層、又はCCDの平坦化層、及び中間層及び保護層の形成に際し特に有用である。又、当該樹脂組成物の熱硬化時や、後工程での工程汚染が極めて少ないので、低コストで信頼性の高い透明薄膜を得ることが出来、得られたカラーフィルター、固体撮像素子は優れた表示品位を確保する事が出来る。又、この透明薄膜を設けたカラーフィルターは、優れた光学特性及び電気特性を有し、このカラーフィルターを用いることによって、高品質なカラー表示装置や固体撮像素子を提供することが出来る。

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(22)Date of filing : 04.03.1999 (72)Inventor : IMAIZUMI NAOKO
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(54) RESIN COMPOSITION FOR TRANSPARENT THIN MEMBRANE AND ITS CURED MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition excellent in preservation stability, and showing less process soiling in its use and a good working efficiency by containing a compound containing glycidyl group and a compound containing an acid anhydride.

SOLUTION: This resin composition is obtained by containing (A) a compound having preferably 5,000–1,000,000 weight-average molecular weight (based on a polystyrene, using a gel permeation chromatography method) and 150–2,000 g/eq epoxy equivalent (JIS K-7236), (e.g.; a high molecular weight epoxy resin) with (B) a compound having preferably 500–500,000 weight-average molecular weight (based on a polystyrene) and containing an acid anhydride in a ratio of (the epoxy equivalent of the component A)/(the acid anhydride equivalent of the component B)=0.2–5. As the component B, a (co)polymer having a compound such as maleic anhydride, itaconic acid anhydride, himic acid anhydride, succinic acid anhydride, etc., as a constituting unit is cited.

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CLAIMS

[Claim(s)]

[Claim 1] The resin constituent for transparency thin films containing the macromolecule (A) which has a glycidyl group, and the macromolecule (B) which has an acid anhydride.

[Claim 2] The resin constituent for transparency thin films according to claim 1 whose weight per epoxy equivalent (WPE) the weight average molecular weight of the macromolecule (A) which has a glycidyl group is 5,000–1,000,000, and is 150–2,000.

[Claim 3] The resin constituent for transparency thin films according to claim 1 or 2 whose weight average molecular weight of the macromolecule (B) which has an acid anhydride is 500–500,000.

[Claim 4] The hardened material of the resin constituent for transparency thin films given in claim 1 thru/or any 1 term of 3.

[Claim 5] The solid state image sensor which has the layer of a hardened material according to claim 4.

[Claim 6] The color filter which has the layer of a hardened material according to claim 4.

[Claim 7] The color liquid crystal display which has a color filter according to claim 6.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the resin constituent for transparency thin films useful as an ingredient which forms the interlayer of the color filter section prepared the flattening layer of a color filter required for specific colorization of a liquid crystal display etc., and the solid state image sensor which makes a color CCD (charge-coupled device) representation, and on it, and a protective layer about the resin constituent for transparency thin films, and its hardened material.

[0002]

[Description of the Prior Art] The flattening layer and the color filter are prepared in the solid state image sensor which makes representation the charge-coupled device in which an application spreads as input devices, such as an image processing system of the color liquid crystal display used for color displays, such as a personal computer, a car-navigation system, and a liquid crystal television, and a video camera, a digital camera, a color copier, and medical equipment in order to ease the irregularity by the solid state image sensor surface light sensing portion, the circuit wiring section, etc. The transparency thin film is formed in the resist-printing interlayer for the color mixture prevention in the protective layer on the color pixel by which patterning was carried out to the predetermined configuration prepared in this flattening layer and color filter, and a staining technique color filter, and the protective layer to protect the front face of each color pixel.

[0003] Conventionally, the photopolymer, the epoxy resin, etc. are used as resin for such a flattening layer, an interlayer, and protective layers. Although carry out UV irradiation of the low-molecular monomer, it is made to construct a bridge and is made to insolubilize in a negative-mold photopolymer. On the other hand from neither the ingredient which becomes the base being low-molecular, nor crosslinking density being obtained enough, the obtained thin film in a positive type photopolymer. The thermal resistance of the thin film obtained by them since it was a straight chain mold macromolecule without bridge formation. Since it was inferior to the thin film obtained from usual thermosetting resin, in case chemical resistance, a water resisting property, a mechanical strength, etc. form transparent electrodes, such as ITO, by elevated-temperature vacuum evaporation, they cause membranous color queerness and wrinkle approach, and might reduce the quality of a color filter remarkably.

[0004] Moreover, since it excelled in thermal resistance and the amine of low molecular weight, an acid anhydride, and imidazole derivatives were used for the curing agent as epoxy system resin used widely, these constituents needed to mix 2 liquid of base resin and a curing agent just before that pot life is short and handling has constraint or spreading. Moreover, the curing agent of low molecular weight volatilized at the time of heat curing, the problem of process contamination of polluting Rhine and a device arose, and the great bad influence is done in respect of productivity, cost, and an environment. Furthermore, by shortening of the postbake time amount accompanying the need for the improvement in a throughout, when the flattening film of CCD, the interlayer of a color filter, and a protective coat are formed with this constituent, since hardening is inadequate, the fault in which an unreacted curing agent is eluted at degree process is also held.

[0005] On the other hand, the conventional typical staining technique color filter for CCD is

created after forming the polymer layer aiming at flattening on an image sensor by repeating the process of preparing the dyeing layer patterned on it, making a resist-printing interlayer transparent subsequently forming, and forming the following dyeing layer similarly on it. As resin which forms this middle class, the reactant of metacrylic acid acrylate (meta), acrylic-acid (meta) 2-hydroxyethyl and cinnamic acid chloride, or its derivative in the giant molecule (JP.61-180235,A) which carried out radical copolymerization, and the interlayer who formed from these although polymethylmethacrylate etc. was known in a former macromolecule, since the color mixture between dyeing layers arises or an adhesive property with a dyeing layer is inferior in a latter macromolecule, the high interlayer of both practicality cannot be obtained. [0006]

[Problem(s) to be Solved by the Invention] This invention is excellent in preservation stability, there is very little process contamination at the time of use, it offers the good resin constituent for transparency thin films of workability, and aims at offering the hardened material of the resin constituent for transparency thin films which was further excellent in thermal resistance, chemical resistance, a water resisting property, resist-printing nature, and adhesion.

[0007]

[Means for Solving the Problem] The resin constituent for transparency thin films with which this invention contains the macromolecule (A) which has (1) glycidyl group, and the macromolecule (B) which has an acid anhydride. The resin constituent for transparency thin films given in (1) (2) and (A) are [weight average molecular weight 5,000-1,000,000 and given weight per epoxy equivalent (WPE)] 150-2,000, (1) (3) and whose (B) are weight average molecular weight 500-500,000, or the resin constituent for transparency thin films given in any 1 term of (3). It is related with the solid state image sensor which has the layer of the hardened material of a publication in (5) and (4), the color filter which has the layer of the hardened material of a publication in (6) and (4), and the color liquid crystal display which has the color filter of a publication in (7) and (6).

[0008]

[Embodiment of the Invention] The resin constituent for transparency thin films of this invention contains the macromolecule (A) which has a glycidyl group, and the macromolecule (B) which has an acid anhydride. As a (A) component used for this invention, the polymer (\rightarrow) of the monomer which has an ethylene nature partial saturation radical and a glycidyl group, and the epoxy resin of the amount of macromolecules are desirable. (A) the weight average molecular weight (MW) of a component — polystyrene conversion — 5,000-1,000,000 — it is 30,000-500,000 preferably. The viscosity of a constituent can also be adjusted by combining two or more sorts of (A) components from which MW differs, weight average molecular weight — gel permeation chromatography (GPC) — it is measured by law. When MW is less than 5,000, it is difficult for the hardening film to be inferior to chemical resistance and a water resisting property, and use it with the practical use level. Although the mechanical strength of the hardening film, chemical resistance, and a water resisting property increase when MW exceeds 1,000,000, since a resin constituent serves as hyperviscosity remarkably, difficulty is caused to thin film-ization. Moreover, 150-2,000 g/eq is desirable still more desirable, and the weight per epoxy equivalent (WPE) of the (A) component is 150-750 g/eq. Weight per epoxy equivalent is JIS. It is measured by the approach of K-7238.

[0009] (A) as a monomer which has the ethylene nature partial saturation radical which is the constituent of the polymer (\rightarrow) of a component, and a glycidyl group For example, (meta), metacrylic acid acrylate, alpha-ethyl metacrylic acid acrylate, Alpha- α -propyl metacrylic acid acrylate, alpha- β -butyl metacrylic acid acrylate. The acrylic ester which has a glycidyl group into ester parts, such as an acrylic acid -3,4-epoxy butyl, an acrylic acid (meta)-4, and 5-epoxy pentyl, (Meta) Methyl glycidyl psychic medium NATO allyl glycidyl ether and ρ -vinyl benzoic-acid glycidyl — Ethyl glycidyl maleate, a vinyl glycidyl sulfonate, glycidyl-beta-vinyl acrylate. Glycidyl diene carboxylate, such as a glycidyl sorbate, the reactant monomer obtained by carrying out the Diels-Alder reaction of a dienophile compound and a diene compound with a

glycidyl group are mentioned.

[0010] The monomer which has an ethylene nature partial saturation radical, for example as the monomer and the monomer which can be copolymerized which has an ethylene nature partial saturation radical and a glycidyl group is mentioned. Specifically, acrylic-acid (meta) alkyl ester, acrylic-acid (meta) dicyclopentan, fumaric-acid alkyl ester, styrene, alpha-alkyl styrene, acrylonitrile, an isobutylene, a butadiene, an isoprene, vinyl acetate, divinyl butyl, etc. are mentioned.

[0011] (A) As an epoxy resin of the amount of giant molecules of a component, the bisphenol A epoxy resin, a bisphenol female mold epoxy resin, a bisphenol smooth S form epoxy resin, a novolak mold epoxy resin, and a glycidyl ether system epoxy resin are mentioned, for example.

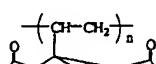
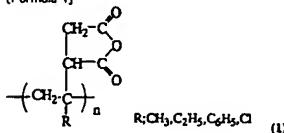
[0012] These (A) components may be used independently, or two or more sorts may be mixed and they may be used.

[0013] As the transparency which is the demand characteristics of this application, thermochromism, and a giant molecule especially desirable as what is excellent in resist-printing nature at the time of dyeing, they are a (glycidyl methacrylate)-(alkyl methacrylate ester) copolymer, a (glycidyl methacrylate)-(styrene) copolymer, and (glycidyl methacrylate) among these, -(alkyl methacrylate ester)-(styrene) It is a copolymer. 1-8 carbon numbers of an alkyl chain are 1-3 pieces preferably. As an example of this compound, there are MAPU roof G-2050M, G-8705, G-1010S, BUREMMA CP-510SA (all are the Nippon Oil & Fats make and trade name), etc.

[0014] As a (B) component used for this invention, the polymer which makes a configuration unit one sort or the compound chosen two or more sorts from a maleic-acid anhydride, an itaconic-acid anhydride, hemic acid anhydride, a succinic-acid anhydride, a citraconic-acid anhydride, an acrylic-acid anhydride, a methacrylic-acid anhydride, etc. (\leftrightarrow) is mentioned. Moreover, as a compound which has the partial saturation double bond in which those and copolymerization are possible, ethylene, propylenes, butene, butadienes, high-class olefins, styrene, stilbenes, vinyl acetate, the alkyl compound ether, 1-methyl cyclopropane, an annular diene compound, a JISHIKURO diene compound, etc. are mentioned, and the good copolymer of alternation nature is obtained. Moreover, the high molecular compound which acid anhydrides, such as a polymeric with the third class hydrogen, a maleic-acid anhydride, a pyromellitic acid anhydride, trimellitic anhydride, a benzophenone tetracarboxylic acid anhydride, a methacrylic-acid anhydride and ethylene glycol bis(trimellitate), and glycerin tri(trimellitate), were made to react, and introduced acid-anhydride structure is mentioned. For example, the compound (**-izing, 70 and 1432, 67) of the following chemical formula (1) and the compound (Pure Appl.Chem., 34 and 305, 73) of the following chemical formula (2) can be mentioned.

[0015]

[Formula 1]



[0016] (B) the weight average molecular weight (MW) of a component — polyatrylene conversion — 500-500,000 — it is 500-300,000 preferably.

[0017] These (B) components may be used independently, or two or more sorts may be mixed and they may be used.

[0018] Although (A) of the resin constituent for transparency thin films of this invention and the loadings of the (B) component may determine a compounding ratio from the physical properties of a hardened material, the range of WPE/acid anhydride equivalent = 0.2-5 has WPE of (A), and the desirable relation of the acid anhydride equivalent of (B). (A) To a component, if there are extremely few loadings of the (B) component, sufficient degree of hardness for a hardened material will not be obtained, or the problem of machine impact nature falling will be produced. On the other hand, since an acid anhydride tends to absorb moisture the moisture in atmospheric air when there are extremely many loadings of the (B) component, the inclination for hardening to be insufficient is caused to the (A) component and also faults, such as nebula of a hardened material, are produced, it is not suitable.

[0019] As occasion demands, the resin constituent for transparency thin film of this invention may add polyamides and a malamine derivative as a hardening agent. As for the amount used, it is desirable that it is extent which does not carry out extensive volatilization at the time of heat hardening, and it is desirable to (A) and (B) sum total solid content, (10% or less of)

[0020] As for the resin constituent for transparency thin films of this invention, it is desirable to prepare as coating liquid dissolved in the solvent. As long as there is no possibility of causing a resin constituent and a chemical reaction as a solvent to be used, there is especially no limit, for example, organic solvents, such as an ester system, an ether system, a ketone system, and an aromatic hydrocarbon system, are mentioned.

[0021] Specifically Acetic-acid alkyl ester, propionic-acid alkyl ester, Saturate aliphatic series monocarboxylic acid alkyl ester, such as butanoic acid alkyl ester Lactic-acid alkyl ester, Alkoxycetic-acid alkyl ester, and 2-hydroxypropanoic acid alkyl ester 2-alkoxy propionic-acid alkyl ester and 3-oxo-propionic-acid alkyl ester 3-alkoxy propionic-acid alkyl ester and 2-oxo-2-methyl propionic-acid alkyl ester 2-methoxy propionic-acid alkyl ester, pyruvric-acid alkyl ester Keto acid ester, such as acetoacetic-acid alkyl ester and 2-oxo-butanic acid alkyl ester Ether, such as the dialkyl ether a tetrahydrofuran, and dioxane, The diethylene-glycol monomethyl ether, diethylene-glycol monoethyl ether, The diethylene-glycol monobutyl ether, ethylene glycol monomethyl ether, Ethylene glycol mono-isopropyl ether, propylene glycol monomethyl ether, Glycol ether, such as the propylene glycol monoethyl ether, and the glycol ether acetate of the stearic Aromatic hydrocarbon, such as ketones, such as a methyl ethyl ketone, a cyclohexanone, 2-heptanone, and 3-heptanone, a xylene, and toluene, is mentioned. These solvents may be used independently, or two or more sorts may be mixed and they may be used.

[0022] In case the resin constituent for transparency thin films of this invention is prepared, in order to raise the physical properties of a paint film, adjustment additive, such as a surface lubricating agent, substrate adhesion amelioration material, and a surfactant, may be added. Specifically, a perfluoroalkyl system compound, a silicon system compound, a polyoxyethylene compound, a polyoxypropylene system compound, a long-chain alkyl compound, etc. are mentioned.

[0023] What is necessary is to add a hardening accelerator and an additive by request further, and just to carry out the mixed dissolution of (A) and the (B) component into the above-mentioned solvent, at homogeneity, in order to prepare the resin constituent for transparency thin films of this invention. The sum density of the (A) component in a solution and the (B) component is about 5-20 % of the weight preferably three to 30% of the weight.

[0024] The hardened material of this invention is applied to a predetermined base material, and is usually formed by carrying out heating baking as a transparency thin film of about 0.05-5 micrometers of thickness. The coloring resin film with which the silicon wafer with which glass, polycarbonates, films, and an image sensor were formed, LCD, or the color filter for CCD was patterned as a base material which should form a transparency thin film, for example, a print sheet, the fiber for printing, a metal plate, etc., are mentioned. As the coating approach, a resin constituent solution is applied on the target base material by approaches, such as a spin coat method, the roll coat method, the bar coat method, print processes, dip coating, and a spray method. Then, heating baking is carried out about 3 to 30 minutes at 180-250 degrees C after predrying about 1 to 10 minutes with the hot plate or convection oven set as 60-120 degrees C, and the hardening film is obtained.

[0025] The color filter of this invention has the hardening film of the above-mentioned constituent. This color filter is used for a color liquid crystal display and a color CCD. Manufacture of the color filter for liquid crystal displays is performed by the well-known approach. For example, the red, blue, green coloring pixel, and black matrix creation-back is formed on a glass substrate, a transparency protective coat is formed on it with the photolithography method, print processes, an electrodeposition process, etc., and it is obtained by carrying out the laminating of the transparency electric conduction film (electrode) of ITO further. By arranging this color filter to the screen, the color liquid crystal display of this invention is obtained.

[0026] The solid state image sensor of this invention prepares the layer of the hardened material of the above-mentioned resin constituent for transparency thin films in the silicon wafer with which the image sensor was formed through direct or other layers. How for the process to form beforehand the color filter which has the layer of the hardened material of the above-mentioned resin constituent for transparency thin films on a glass substrate, cut this to a chip size, and stick with adhesives after alignment on a CCD chip. On the silicon substrate in which the solid state camera which changes by the optoelectric transducer, a charge coupled device, etc. was formed the layer of the hardened material of the above-mentioned resin constituent for transparency thin films is formed for smoothing of the irregularity on the front face of a silicon wafer, next, a direct color filter is formed by the staining technique or the pigment-content powder photolithography method, and there is the method on chip cut for the chip after color filter completion. The manufacture approach of the latter which is excellent in alignment precision and mass-production nature is in use. The color filter in the former approach is the same as that of the process of the color filter for LCD. The latter process forms a transparency thin film first for smoothing of the irregularity on the front face of a silicon wafer, when creating a color pixel by the staining technique next, it forms the transparency thin film for the purpose of resist printing after each color dyeing color, and the color filter of CCD completes it by preparing a protective layer with a transparency thin film after the last color pixel dyeing.

[0027] Since the aforementioned (A) component and the (B) component construct a bridge for each other and the resin constituent for transparency thin films of this invention ultrahigh-molecular-weightizes by heat-treating as mentioned above, the obtained transparency thin film is excellent in thermal resistance, chemical resistance, a water resisting property, a dye affinity-proof, and adhesion, and becomes useful especially on the occasion of formation of the protective layer of coloring resin film, such as a color filter for LCD, or the flattening layer of CCD, an interlayer, and a protective layer. Moreover, since a low molecular weight compound is not included, the liquid crystal display which used the color filter with which process contamination, such as volatilization and elution, obtained the transparency thin film with very little high dependency, and was obtained by this, and the solid state image sensor can secure the outstanding display grace.

[0028]

[Example] Although an example explains this invention still more concretely, this invention is not limited only to these examples.

[0029] It dissolved so that it might become propylene-glycol-monomethyl-ether acetate with

11 % of the weight of solid content by the ratio which shows respectively the copolymerization high molecular compound of the (A) group shown in one to example 10 table 1, and the high molecular compound of the (B) group in Table 2, and the resin constituent for transparency thin film was prepared.

[0030]

table 1 (A) Group MW WPE (B) Group MW a1 G-2050M 225,000 340 b1 GSM-1001 10,000 a2-GMA-MMA- 100,000 240 b2 GSM-6001 60,000 a3 -GMA-BMA- 300,000 1000 b3 GSM-1001 100,000 a4-GMA-AN- 150,000 500 b4 Formula (1) 50,000 a5 -GMA-ST- 400,000 2500 b5 Formula (2) 25,000 [0031] However, GMA; glycidyl methacrylate, MMA; methyl methacrylate, G-2050 M;GMA-MMA copolymer (Nippon Oil & Fats make, trade name), BMA; butyl methacrylate, AN; acrylonitrile, ST; styrene, and GSM-1001; styrene-maleic-acid anhydride 1:1 copolymer (the product made from the Gifu shellac, trade name), GSM-6001; styrene-maleic-acid anhydride 1:1 copolymer (the product made from the Gifu shellac, trade name), GSM-1001; styrene-maleic-acid anhydride 1:1 copolymer (the product made from the Gifu shellac, trade name) is expressed.

[0032]

Table 2 Example a1 a2 a3 a4 a5 b1 b2 b3 b4 b5 1 10 3 2 10 4 3 10 2 4 10 35 10 2 6 10 2 7 10 38 10 2 9 10 310 103 (solid weight ratio)

[0033] It carried out so that evaluation of the solvent resistance of the hardening film obtained with these various resin constituents for transparency thin films, a water resisting property, thermal resistance, *****, and residue contamination might be described below. An evaluation result is shown in Table 5.

[0034] It applied so that it might become the 0.5 micrometers of the last thickness on the example glass substrate of creation of the hardening film of the resin constituent for transparency thin films, and it heated for 5 minutes on the 200-degree C hot plate after predrying for 100 seconds on the hot plate with a skin temperature of 100 degrees C, and the transparency thin film was obtained. Let this be various test pieces.

[0035] Solvent resistance: The thickness before and behind processing and a trial was measured for the above-mentioned test piece on various conditions to the following solvent, it asked for the remaining ratio of membrane, and the film surface was observed with the optical microscope.

** 60 degree-CIPA (isopropanol) steamy x20 minute exposure **50 degree-CNMP(N-methyl pyrrolidone) x20 minute immersion **50 degree-CGBL(gamma-butyrolactone) x20 minute immersion [0036] Water resisting property: The above-mentioned test piece was put into the container for a pressure cooker trial (PCT) containing pure water, processing was performed at 130 degrees C for 3 hours, and the film surface was observed with the optical microscope.

[0037] Thermal resistance: The above-mentioned test piece was heat-treated for 80 minutes with the 250-degree C hot plate, and whenever [before and behind heating / coloring] (deltaE*ab value; chromaticity difference) was measured with the spectrophotometer.

[0038] The ***** and transparency thin film top of the residue contamination above —— pigment-content powder color NEGAREJISUTO KAYAMIRROR DCF-G630 (green-pigments resist; — the Nippon Kayaku make —) A trade name is applied to thickness by about 1 micrometer. On a 80-degree C hot plate. After the prebake during 100 seconds, it is KAYAMIRROR with ultraviolet-rays λ -irradiating. Negatives were completely developed in DVL-T50D (organic alkali system developer; the Nippon Kayaku make, trade name), and ***** (deltaE*ab value) to an after [rinsing desiccation] transparency thin film top was measured with the spectrophotometer. Moreover, the microscope estimated residue contamination.

[0039] It dissolved in the solvent so that it might become 11 % of the weight of solid content with the compounding ratio shown in Table 4 as a resin constituent for transparency thin films which combined the thermosetting resin shown in one to example of comparison 3 table 3, and a curing agent. Evaluation of solvent resistance, a water resisting property, thermal resistance, *****, and residue contamination was performed like the above. An evaluation result is shown in Table 5.

[0040]

table 3 Thermosetting resin MW WPE Curing agent c1 -GMA-MMA- 100,000 240 d1 Trimellitic anhydride c2 -GMA-MMA- 225,000 340 d2 Tetrahydro phthalic anhydride c3 -MAA-(N-phenyl m- imide- :imide-) 10,000 300 d3 IRGANOX 3114 [0041] However, IRGANOX3114; tri-(3, 5-G-t-butyl-4-hydroxybenzyl)- isocyanurite (the Ciba-Geigy make, trade name)

[0042] table 4 Example of a comparison c1 c2 c3 d1 d2 d3 1 10 1 2 10 1.5 3 10 1 0.5 (solid weight ratio)

[0043]

table 5 Solvent resistance (remaining rate of membrane) Deck watertight luminesce Heatproof ***** Example IPA NMP GBL PCT Delta*ab delta*ab Residue 1 100% 100% 100% What 0.1 0.1 Nothing 2 100% 100% 100% ** 0.2 0.1 Nothing 3 100% 100% 100% 0.3 0.1 Nothing 4 100% 100% Strange 0.4 0.1 Nothing 8 100% 100% 100% -izing 0.1 0.1 Nothing 7 100% 100% 100% Nothing 0.2 0.1 Nothing 8 100% 100% 100% It carries out 0.2 0.1 Nothing The example of a comparison 1 82% 85.83% 0.83.5 ***** 2 88% 80% 85% milkiness 0.7 Those with 5.7 3 77% 70% 2 Milkiness 2.0 6.8 ***** [0044] The resin constituent for transparency thin films of the example 11 above was applied so that it might become the 0.3 micrometers of the last thickness on the silicon wafer with which the image sensor was arranged, and it was heated for 5 minutes on the 200-degree C hot plate after predrying for 100 seconds on the hot plate with a skin temperature of 100 degrees C, and the substrate flattening film was obtained. On this substrate flattening film, it is pigment-content powder color NEGAREJISUTO KAYAMIRROR, DCF-G630 (green-pigments resist; the Nippon Kayaku make, trade name) was applied to thickness by about 1 micrometer, and the ultraviolet rays of 150mJ/s (365nm) were irradiated through the predetermined pattern photo mask after prebake for 100 seconds on the 80-degree C hot plate. Then, KAYAMIRROR in DVL-T50D (organic alkali system developer; the Nippon Kayaku make, trade name), after development and rinsing desiccation, postbake was carried out for 5 minutes on the 200-degree C hot plate, and the green detailed pixel was formed. Subsequently, pigment-content powder color NEGAREJISUTO KAYAMIRROR DCF-R630 (red-pigments resist; the Nippon Kayaku make, trade name) was applied to thickness by about 1 micrometer, and the ultraviolet rays of 150mJ/s (365nm) were irradiated through the predetermined pattern photo mask after prebake for 100 seconds on the 80-degree C hot plate. Then, KAYAMIRROR Postbake was carried out for 5 minutes on the 200-degree C hot plate after development and rinsing desiccation in DVL-T50D (organic alkali system developer; the Nippon Kayaku make, trade name), the red detailed pixel was formed, and the solid state image sensor with which direct attachment of the color filter was carried out was obtained. When this was observed from right above under the microscope, ***** to a substrate flattening film top and residue contamination were not accepted at all.

[0045] On example 12 glass substrate, it is pigment-content powder color NEGAREJISUTO KAYAMIRROR. On the coloring resin film which carried out pattern formation of the pixel of red, green, and blue by the same approach as an example 11 using DCF-R630, DCF-G630, and DCF-B630 (red, green, blue pigment resist; the Nippon Kayaku make, trade name), with the resin constituent for transparency thin films of examples 1-10, the transparency thin film was formed as a protective coat, and the color filter for LCD was created. When the cross-cut friction test estimated the adhesion of each protective coat, all checked film adhesion by 0/100 exfoliations. Moreover, as for the wrinkle approach phenomenon, neither was seen.

although it applied at 250 degrees C on these color filters for 30 minutes and vacuum

evaporation actuation of ITO was performed.

[0046]

[Effect of the Invention] By using the resin constituent for transparency thin films of this invention, the transparency thin film excellent in thermal resistance, chemical resistance, a water resisting property, a dye affinity-proof, and adhesion can be manufactured simple. Especially on the occasion of formation of the protective layer of the coloring resin film of the color filter for LCD or the flattening layer of CCD, an interlayer, and a protective layer, it is useful. Moreover, since there are very little time of heat curing of the resin constituent concerned and process contamination at a back process, a reliable transparency thin film can be obtained by low cost, and the obtained color filter and a solid state image sensor can secure the outstanding display grace. Moreover, the color filter which prepared this transparency thin film has the outstanding optical property and the outstanding electrical property, and can offer a quality electrochromatic display and a quality solid state image sensor by using this color filter.

[Translation done.]

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